| AD NUMBER |
|---|
| AD504706 |
| **CLASSIFICATION CHANGES** |
| TO: unclassified |
| FROM: confidential |
| **LIMITATION CHANGES** |
| TO: Approved for public release, distribution unlimited |
| FROM: Distribution authorized to U.S. Gov't. agencies and their contractors; Critical Technology; JUL 1969. Other requests shall be referred to Air Force Rocket Propulsion Laboratories, ATTN: RPPR-STINFO, Edwards AFB, CA 93523. |
| **AUTHORITY** |
| 31 Jul 1981, DoDD 5200.10; AFRPL ltr dtd 22 Jan 1986 |

# SECURITY

# MARKING

**The classified or limited status of this report applies to each page, unless otherwise marked.**
**Separate page printouts MUST be marked accordingly.**

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE UNITED STATES WITHIN THE MEANING OF THE ESPIONAGE LAWS, TITLE 18, U.S.C., SECTIONS 793 AND 794. THE TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U.S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

1473

CONFIDENTIAL

18 19 AFRPL-TR-69-183

20

AD504706

AD 504706

AD No. ___

DDC FILE COPY

β

(TITLE UNCLASSIFIED)

6

# INVESTIGATION OF THE THERMODYNAMIC PROPERTIES OF PROPELLANT INGREDIENTS (U).

9 FINAL, progress ~~TECHNICAL~~ REPORT, AFRPL-TR-69-183

1 Jan 67 - 30 Jun 69,

11 JULY 1969

10 G. C. Sinke, J. L. Curnutt, D. R. Stull

12 19p.

DDC
RECEIVED
OCT 6, 1969
D

AIR FORCE ROCKET PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
EDWARDS AIR FORCE BASE, CALIFORNIA

[redacted]

14 T-0025-F-69

16 AF-3148

15

(Prepared under Contract Nr F04611-67-C-0025
The Dow Chemical Company,
Midland, Michigan 48640)

mlk (403 481)

CONFIDENTIAL

## NOTICE

The information in this report is presented in good faith, but no warranty is made, nor is freedom from any patent to be inferred.

## LEGAL NOTICE

When U. S. Government drawings, specifications, or other data are used for any purpose other than a definitely related Government procurement operation, the Government thereby incurs no responsibility nor any obligation whatsoever, and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not be be regarded by implication or otherwise, or in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may be in any way related thereto.

## SECURITY NOTICE

This document contains information affecting the National Defense of the United States within the meaning of the espionage laws (Title 18, U.S.C., Sections 793 and 794). Transmission or revelation in any manner to a unauthorized person is prohibited by law.

## DISTRIBUTION

Distribution has been made in accordance with the automatic distribution list, plus Category B-2 of the CPIA Publication No. 147, Chemical Propulsion List, May, 1967, with subsequent changes.

 CONFIDENTIAL

AFRPL-TR-69-183

THIS MATERIAL CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE UNITED STATES WITHIN THE MEANING OF THE ESPIONAGE LAWS, TITLE 18, U. S. C., SECS. 793 AND 794, THE TRANSMISSION OR REVELATION OF WHICH IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.

This document consists of 24 pages, copy [redacted] of 142 copies.

Report Nr. T0025-F-69

# FINAL PROGRESS REPORT (U)

July 1969

AIR FORCE SYSTEMS COMMAND
RESEARCH AND TECHNOLOGY DIVISION
ROCKET PROPULSION LABORATORY
EDWARDS, CALIFORNIA 93523
CONTRACT NR. F04611-67-C-0025

In addition to security requirements which must be met this document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of AFRPL (RPPR-STINFO), Edwards, California 93523.

DOWNGRADED AT 3 YEAR INTERVALS; DECLASSIFIED AFTER 12 YEARS
DOD DIR 5200.10

CHEMICALS LABORATORY
THE DOW CHEMICAL COMPANY
MIDLAND, MICHIGAN 48640

m 4 (403 481)

 CONFIDENTIAL

## FOREWORD

This report was prepared by The Dow Chemical Company, Midland, Michigan, under USAF Contract F04611-67-C-0025. The contract was initiated under Air Force Program 750 G, AFSC Project 3148, "Investigation of the Thermodynamic Properties of Propellant Ingredients and the Burning Mechanisms of Propellants." The work was administered under the direction of the Rocket Propulsion Laboratory, Edwards Air Force Base, with Mr. Curtis C. Selph acting as Air Force Project Officer.

This final report covers the work performed during 1 January 1967 through 30 June 1969. The Dow Report Number is T0025-F-69.

This work was performed by Dr. G. C. Sinke and Dr. J. L. Curnutt, under the technical supervision of Dr. D. R. Stull and Dr. H. Prophet and management supervision of Dr. K. O. Groves.

This report has been reviewed and is approved.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

ABSTRACT

(C) The heats of formation of methylene bisoxyamine ($CH_6N_2O_2$) and methylene bisoxyamine diperchlorate ($CH_6N_2O_2 \cdot 2HClO_4$) were derived from oxygen bomb combustion calorimetry and solution calorimetry. Selected best values for the two compounds are -22.4 kcal/mole for liquid methylene bisoxyamine and -103.0 kcal/mole for crystalline methylene bisoxyamine diperchlorate.

(C) A technique for obtaining heats of formation of gaseous C-H-O-N-F compounds was developed, with $CF_3CN$ as a reference substance. When the technique was applied to $F_2C(ONF_2)_2$, results deviated widely from the expected range. Chromatographic examination revealed a large fraction of $F_3CONF_2$ was present in the sample and no accurate result for $F_2C(ONF_2)_2$ could be derived. The amount of sample available was too small to allow purification.

TABLE OF CONTENTS

# (U) THERMOCHEMISTRY

## A. THE HEATS OF FORMATION OF METHYLENE BISOXYAMINE AND METHYLENE BISOXYAMINE DIPERCHLORATE (C)

### 1. Introduction (U)

(C) Samples of methylene bisoxyamine (hereafter referred to by code letters DO) and methylene bisoxyamine diperchlorate (code letters DOAP) were received from Dr. Claude Merrill of the Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, California. The samples were investigated by both oxygen bomb and solution calorimetry.

### 2. Materials (U)

(U) DO is a colorless liquid, reported by AFRPL to be flammable and to have an impact sensitivity of 70 kg-cm and a vapor pressure of 1 mm at 33°C. It is somewhat hygroscopic and was transferred only in a dry nitrogen atmosphere. It is decomposed catalytically by a number of substances. The present sample was stated on the basis of vapor phase chromatography to be of higher purity than the 99.1% material for which data were reported earlier (1).

(U) DOAP was a white crystalline solid. According to Dr. Merrill, elemental analyses for carbon, hydrogen, and nitrogen were in good accord with theory. The compound was transferred only in a dry nitrogen atmosphere. An analysis for perchlorate ion at Dow gave 71.15% $ClO_4^-$ versus theory of 71.29%.

(U) Ethylene glycol was used as a solvent for both DO and DOAP. The glycol is hygroscopic and between the two investigations it picked up enough water to change its heat of combustion appreciably. The heat of combustion of the glycol was therefore measured twice, once at the time of DO experiments and once at the time of the DOAP experiments.

### 3. Equipment (U)

(U) A rotating bomb calorimeter and a platinum-lined bomb were employed for heat of combustion work. A simple glass Dewar calorimeter was used for heats of solution. A Beckman microcalorimeter was used for the heat of mixing of DO and ethylene glycol.

### 4. Procedure (U)

(U) Preliminary experiments showed both DO and DOAP detonated to incomplete combustion products when ignited in a platinum crucible in a bomb charged with oxygen at 30 atm pressure. Suitable moderation of the combustion reaction was achieved by burning a 50-50 mixture of DO or DOAP with ethylene glycol.

(U) A long narrow bag open on both ends was fabricated from 0.5 mil polypropylene film and accurately weighed. A clamp was fastened across the middle of the bag and the assembly weighed. An appropriate amount of DO or DOAP was added to one side of the bag; this transfer was carried out in a dry nitrogen atmosphere. The end of the bag was heat sealed, and the bag assembly was removed from the dry box and weighed to determine the amount of DO or DOAP added. Ethylene glycol was then added to the other side of the bag, which was heat sealed and weighed to determine the exact amount of glycol added. After visual inspection and absence of weight loss had established that the bag was not leaking, the clamp was removed and the contents of the bag mixed by gentle manipulation.

(U) The bag was next folded into a platinum crucible which was suspended in a gimbal in the combustion bomb. A cotton thread fuse was strung from a fine platinum ignition wire to the bag. For DO experiments, 1.0 ml of water was added to the bomb; for DOAP runs, approximately 11 g of 0.08 M $As_2O_3$ solution was added from a weight buret. The bomb was closed and charged with purified oxygen to 30 atm pressure. After thermal equilibrium was established, the charge was fired by electrical heating of the fuse wire, and the resulting temperature rise was accurately monitored by an automatic resistance bridge. After the calorimetry the bomb was slowly discharged, opened, and washed out with hot distilled water. The washings were analyzed for nitrate and, in the case of DOAP, also for $As_2O_3$ and dissolved platinum.

(U) The heat of combustion of ethylene glycol was measured in the same apparatus. The conditions for the glycol experiments (such as loading and weighing times) were kept as nearly as possible identical to the DO-glycol experiments to eliminate systematic errors. The heats of combustion of the polypropylene film and cotton fuse were reported earlier (1).

(U) Heats of mixing of DO and DOAP in 1 N perchloric acid were measured in a simple Dewar vessel calorimeter equipped with a heater, stirrer, and thermometer. Samples of 1 to 2 g were sealed in thin walled glass ampoules which were immersed in 1 liter of aqueous acid. After thermal equilibrium had been established, the ampoule was broken by means of a push rod and the resulting temperature change recorded. The calorimeter was calibrated by addition of electrical energy. The heat of mixing of DOAP and ethylene glycol was derived from measurements of the heats of solution of DOAP, ethylene glycol, and of the 50-50 DOAP-glycol mixture in aqueous 1 N perchloric acid.

(U) The heat of mixing of DO and ethylene glycol was observed directly in a Beckman microcalorimeter (1).

5. Calculations (U)

(U) A number of corrections must be applied to the bomb calorimeter data in order to derive true heats of formation. These corrections are calculated by means of a computer program based on the outline of Hubbard et al. (2) for C-H-O and C-H-O-N compounds and of Baroody et al. (3) for C-H-O-N-Cl compounds. Parameters for C-H-O-N compounds are reasonably well established, but for C-H-O-N-Cl some estimates have to be made (4). Constant factors specific for the individual compounds DO, DOAP, and glycol are given in Table I.

(U) The calorimeter equivalents, E (calor), were determined by combustion of benzoic acid and are averages of numerous determinations.

6. Results (U)

(C) Calorimetric data for methylene bisoxyamine are given in Table II. The correction for ethylene glycol is taken from data in Table III.

(C) To the average result of Table II is added the heat of mixing of 5.3 cal/g to give $-\Delta E^\circ_c/M = 3539.0$ cal/g. The molecular weight of methylene bisoxyamine is 78.071 which yields:

$$\Delta E^\circ_{c\,298} = 276.29 \pm 0.37 \text{ kcal/mole}$$

for the reaction:

$$CH_6N_2O_2(\ell) + 3/2\ O_2(g) \rightarrow CO_2(g) + 3H_2O(\ell) + N_2(g)$$

Calculating to constant pressure conditions:

$$\Delta H^\circ_{c\,298} = -276.59 \pm 0.37 \text{ kcal/mole}$$

from which is derived:

$$\Delta Hf^\circ_{298}(\ell) = -22.4 \pm 0.37 \text{ kcal/mole}$$

The uncertainty is twice the standard deviation.

(C) Calorimetric data for methylene bisoxyamine diperchlorate are given in Table IV. Correction for ethylene glycol is based on data in Table V. The average result of Table IV and a molecular weight of 278.988 yield:

$$\Delta E^\circ_c = -276.86 \pm 1.48 \text{ kcal/mole}$$

for the reaction:

$$CH_8Cl_2N_2O_{10}(\text{in glycol}) \rightarrow CO_2(g) + 2HCl(600H_2O) + 3H_2O(\ell) + N_2(g) + 5/2\ O_2(g)$$

Table I

(C) Constant Factors in Combustion Calorimetry of DO and DOAP[a]

| | |
|---|---|
| Empirical formula, DO | $CH_6N_2O_2$ |
| Empirical formula, DOAP | $CH_8Cl_2N_2O_{10}$ |
| Empirical formula, glycol | $C_2H_6O_2$ |
| Density of DO, g/cc | 1.100 |
| Density of DOAP, g/cc | (1.85) |
| Density of glycol, g/cc | 1.115 |
| Bomb volume, liter | 0.349 |
| Water added to bomb for DO and glycol, ml | 1.0 |
| Initial oxygen pressure at 25°C, atm | 30.3 |
| Reference temperature, °C | 25.00 |
| Final ratio $H_2O/HCl$ for DOAP | 600 |
| $(\partial E/\partial P)_T$ of DO, cal/g/atm | (-0.003) |
| $(\partial E/\partial P)_T$ of DOAP, cal/g/atm | (-0.001) |
| $(\partial E/\partial P)_T$ of glycol, cal/g/atm | -0.00397 |
| $C_p$ of DO, cal/g/°C | (0.50) |
| $C_p$ of DOAP, cal/g/°C | (0.26) |
| $C_p$ of glycol, cal/g/°C | 0.577 |
| E(calor), cal/°C | 3427.20 |
| Added platinum parts, g | 47.33 |

[a]Quantities in parentheses are estimated.

Table II

(C) Combustion Experiments on Methylene Bisoxyamine (DO)

| Parameter | Experiment Number 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| DO mass, g | 0.49928 | 0.51027 | 0.52140 | 0.52723 | 0.52010 |
| Glycol mass, g | 0.83184 | 0.87451 | 0.84927 | 0.85420 | 0.73021 |
| Film mass, g | 0.10389 | 0.09705 | 0.10592 | 0.10240 | 0.12076 |
| Fuse mass, g | 0.00386 | 0.00301 | 0.00365 | 0.00379 | 0.00385 |
| $t_i$, °C | 22.96676 | 22.96674 | 22.96672 | 22.96670 | 22.96674 |
| $t_f$, °C | 24.98489 | 25.02581 | 25.03119 | 25.03107 | 24.93344 |
| $\Delta t_{corr.}$, °C | 0.06858 | 0.06530 | 0.06176 | 0.06159 | 0.07397 |
| $\mathcal{E}_i$ (cont.), cal/°C | 5.658 | 5.684 | 5.680 | 5.684 | 5.649 |
| $\mathcal{E}_f$ (cont.), cal/°C | 6.179 | 6.215 | 5.924 | 5.934 | 5.865 |
| Corr. to std. states, cal[a] | 3.114 | 3.226 | 3.220 | 3.202 | 2.954 |
| Ignition energy, cal | 0.36 | 0.36 | 0.32 | 0.37 | 0.41 |
| $\Delta E_{HNO_3}$, cal | 12.456 | 12.244 | 12.244 | 14.215 | 12.104 |
| $-\Delta E_c^\circ/M$, cal/g | 3533.8 | 3534.1 | 3542.2 | 3530.4 | 3528.1 |

Average $-\Delta E_c^\circ/M = 3533.7$ cal/g, $\sigma = 2.4$ cal/g

[a]Includes Items 81-85 and 87-94 of Reference 2.

Table III

(U) Heat of Combustion of Ethylene Glycol for DO Experiments

| Parameter | Experiment Number 9 | 10 | 11 |
|---|---|---|---|
| Sample mass, g | 1.38125 | 1.39260 | 1.36154 |
| Polypropylene, g | 0.07482 | 0.07219 | 0.09922 |
| Cotton fuse, g | 0.00362 | 0.00318 | 0.00236 |
| $t_i$, °C | 22.96679 | 22.96664 | 22.96676 |
| $t_f$, °C | 25.08628 | 25.09333 | 25.13661 |
| $\Delta t_{corr}$, °C | 0.06020 | 0.06252 | 0.05671 |
| Ign. Energy, cal | 0.36 | 0.36 | 0.38 |
| Corr. to std. states, cal[a] | 3.561 | 3.581 | 3.612 |
| $\mathcal{E}_i$(cont.), cal/°C | 5.701 | 5.707 | 5.727 |
| $\mathcal{E}_f$(cont.), cal/°C | 6.231 | 6.237 | 6.274 |
| $-\Delta E_{\mathcal{B}}/M$, cal/g | 4504.9 | 4502.4 | 4503.5 |

[a] Includes Items 81-85 and 87-94 of Reference 2.

Table IV

(C) Heat of Combustion of Methylene Bisoxyamine Diperchlorate

| Parameter | Experiment Number 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Sample mass, g | 0.50090 | 0.49822 | 0.51089 | 0.49928 | 0.50170 |
| Glycol mass, g | 1.21373 | 1.09178 | 1.13825 | 1.14813 | 1.14898 |
| Polypropylene mass, g | 0.09441 | 0.09461 | 0.07988 | 0.08772 | 0.09170 |
| Cotton fuse mass, g | 0.00442 | 0.00387 | 0.00344 | 0.00408 | 0.00340 |
| $n^i$ ($H_2O$), mole | 0.6522 | 0.5952 | 0.6410 | 0.6116 | 0.6169 |
| $n^i$ ($As_2O_3$), mole | 0.001243 | 0.001135 | 0.001227 | 0.001170 | 0.001174 |
| $n^f$ ($As_2O_3$), mole | 0.001162 | 0.001019 | 0.001144 | 0.001106 | 0.001125 |
| $n^f$ ($HNO_3$), mole | 0.000516 | 0.000520 | 0.000508 | 0.000504 | 0.000540 |
| $n^f$ ($H_2PtCl_6$), mole | 0.000011 | 0.000011 | 0.000010 | 0.000009 | 0.000007 |
| $t_i$, °C | 22.96678 | 22.96678 | 22.96677 | 22.96033 | 22.96677 |
| $t_f$, °C | 25.08450 | 24.93516 | 24.94820 | 24.97982 | 24.99362 |
| $\Delta t_{corr.}$, °C | 0.06302 | 0.07472 | 0.07138 | 0.07469 | 0.06758 |
| Ign. energy, cal | 0.39 | 0.36 | 0.37 | 0.39 | 0.39 |
| Corr. to std. state, cal[a] | 7.736 | 6.746 | 7.142 | 7.076 | 7.147 |
| $\mathcal{E}_i$(cont.), cal/°C | 16.422 | 15.332 | 16.173 | 15.656 | 15.753 |
| $\mathcal{E}_f$(cont.), cal/°C | 16.821 | 15.685 | 16.534 | 16.031 | 16.136 |
| $-\Delta E_c^\circ/M$, cal/g | 499.2 | 492.5 | 507.4 | 493.6 | 499.2 |

Average $-\Delta E_c^\circ/M$ = 498.4 cal/g, $\sigma$ = 2.6 cal/g

[a]Includes Items 81-85, 87-89, 93, and 94 of Reference 2.

Table V

(U) Heat of Combustion of Ethylene Glycol for DOAP Experiments

| Parameter | Experiment Number 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Sample mass, g | 1.36266 | 1.36609 | 1.35999 | 1.36760 | 1.35481 |
| Polypropylene, g | 0.05588 | 0.06923 | 0.05754 | 0.06102 | 0.06519 |
| Cotton fuse, g | 0.00400 | 0.00378 | 0.00392 | 0.00346 | 0.00400 |
| $t_i$, °C | 22.96673 | 22.96669 | 22.96672 | 22.96684 | 23.00462 |
| $t_f$, °C | 25.01884 | 25.06089 | 25.01880 | 25.03658 | 25.06574 |
| $\Delta t_{corr.}$, °C | 0.06934 | 0.06544 | 0.06950 | 0.06488 | 0.05931 |
| Ign. energy, cal | 0.35 | 0.36 | 0.36 | 0.28 | 0.32 |
| Corr. to std. states, cal[a] | 3.425 | 3.493 | 3.425 | 3.460 | 3.444 |
| $\mathcal{E}_i$(cont.), cal/°C | 5.681 | 5.687 | 5.680 | 5.685 | 5.679 |
| $\mathcal{E}_f$(cont.), cal/°C | 6.186 | 6.206 | 6.186 | 6.197 | 6.191 |
| $-\Delta E_c^\circ/M$, cal/g | 4526.4 | 4523.0 | 4521.6 | 4525.5 | 4524.9 |

Average $-\Delta E_c^\circ/M = 4524.3$ cal/g

[a]Includes Items 81-85 and 87-94 of Reference 2.

Correcting to constant pressure conditions:

$$\Delta Hc^\circ_{298} = -276.86 + 9/2\ RT$$
$$= -274.20 \pm 1.48 \text{ kcal/mole}$$

(C) Before proceeding to heat of formation calculations, the heat of solution results will be presented. Duplicate determinations agreed to within ±0.2 kcal/mole for the following heats of solution in 1 N $HClO_4$:

| | ΔH sol'n, kcal/mole |
|---|---|
| $CH_6N_2O_2(\ell)$ | -13.6 |
| $CH_6N_2O_2 \cdot 2HClO_4(c)$ | + 5.1 |
| Ethylene glycol ($\ell$) | - 1.35 |
| DOAP (dissolved in glycol) | + 6.5 |

The difference in the heat of solution of crystalline DOAP and DOAP dissolved in glycol gives the heat of solution of DOAP in glycol as -1.4 kcal/mole. The heat of combustion of crystalline DOAP is therefore:

$$\Delta Hc^\circ_{298}(c) = -274.20 - 1.40 \text{ kcal/mole}$$
$$= -275.60 \pm 1.48 \text{ kcal/mole}$$

The heat of formation of methylene bisoxyamine perchlorate is calculated from this value and heats of formation of $CO_2$, HCl (in $600H_2O$) and $H_2O$ as:

$$\Delta Hf^\circ_{298}(c) = -103.0 \pm 1.5 \text{ kcal/mole}$$

(C) The above heats of solution provide a cross-check on the heat of combustion results. From National Bureau of Standards Technical Note 270-3 the heat of formation of 1 N $HClO_4$ is -30.96 kcal/mole. The following reaction scheme can be written:

$$CH_6N_2O_2(\ell) + 2HClO_4(aq) \rightarrow [CH_6N_2O_2 \cdot 2HClO_4]\ (aq)$$
$$\Delta H = -13.6 \text{ kcal}$$

$$CH_6N_2O_2 \cdot 2HClO_4(c) \rightarrow [CH_6N_2O_2 \cdot 2HClO_4]\ (aq)$$
$$\Delta H = +5.1 \text{ kcal}$$

adding algebraically:

$$CH_6N_2O_2(\ell) + 2HClO_4(aq) \rightarrow CH_6N_2O_4 \cdot 2HClO_4\ (c)$$
$$\Delta H = -18.7 \text{ kcal}$$

Therefore the difference between the heats of formation of methylene bisoxyamine and its diperchlorate should be:

$$\Delta H = -18.7 + 2(-30.96)$$
$$= -80.6 \text{ kcal}$$

The difference from combustion calorimetry is:

$$\Delta H = -103.0 - (-22.4)$$
$$= -80.6 \text{ kcal}$$

The exact agreement is of course fortuitous, but does demonstrate the consistency of the thermochemical network and indicates the individual values are highly reliable.

## B. ATTEMPTED MEASUREMENT OF THE HEAT OF FORMATION OF $F_2C(ONF_2)_2$ (C)

### 1. Introduction (U)

(C) A one gram sample of $F_2C(ONF_2)_2$ was received from Dr. Pilipovich of Rocketdyne Corporation. According to Dr. Pilipovich, the infrared spectrum of the sample was identical to that of highly pure material he had prepared previously. Because of the limited amount of sample and limited time available, no attempt was made to further establish the purity and the sample was used as received.

### 2. Method (U)

(C) A technique for carrying out an explosion reaction in a combustion bomb, followed by the addition of water to the bomb from an annular tank, was developed some years ago A description of the technique as applied to the reaction of $NF_3$ and $H_2$ has been published (5). For $F_2C(ONF_2)_2$, it was believed that a mixture with $H_2$ and $O_2$ would give an explosive mixture yielding HF, $CO_2$ and $N_2$ with perhaps some $HNO_3$. However, it was found that $H_2$ and $O_2$ react slowly to form water in a platinum lined bomb. A sample of high purity propane was substituted for hydrogen; this had the advantage that the propane could be condensed in a steel cylinder and weighed.

(U) To check out this technique, a sample of high purity $CF_3CN$ was exploded with about an equal amount of propane and a twofold excess of oxygen. Infrared examination of the bomb gases showed only $CO_2$; no trace of $CF_4$ was observed. The heat of the explosion was measured and a heat of formation calculated for $CF_3CN$ in good agreement with a value obtained from the heat of reaction of $CF_3CN$ and $NF_3$ (6). The technique was therefore regarded as satisfactory.

### 3. Results (U)

(C) Two explosions on samples of about 0.3 g were carried out. The heats of reaction were far less than expected for $F_2C(ONF_2)_2$; in addition, the molecular weight of the material

calculated from the pressure, the bomb volume, and the ambient temperature was far below theory. The remaining sample was therefore examined by vapor phase chromatography which showed about 10% of $F_3CONF_2$ to be present. Ordinarily, one might be able to correct for this impurity; however, it appears that the original sample was partially condensed in the steel cylinder and the gas phase was much richer in $F_3CONF_2$ than the liquid. Thus, the first explosion experiment probably involved 50% or more of $F_3CONF_2$, the second about 20%, and the remaining sample still had 10% $F_3CONF_2$. No accurate single composition could therefore be derived. It seems clearly impossible to derive any satisfactory heat of formation from the data obtained.

## REFERENCES


1. The Dow Chemical Company, Midland, Michigan, Annual Progress Report AFRPL-TR-69-31, Contract Nr. F04611-67-C-0025, January, 1969.

2. W. Hubbard, D. W. Scott, and G. Waddington, Chapt. 5 of "Experimental Thermochemistry," Vol. I, Interscience, New York, 1956.

3. E. E. Baroody, G. J. Wynne, and M. F. Zimmer, U. S. Naval Propellant Plant, Indian Head, Md., NavWeps Report 8686, Technical Report 154, August 17, 1964.

4. Reference 1, page 46.

5. G. C. Sinke, J. Chem. Eng. Data, 3, 295 (1965).

6. L. C. Walker, The Dow Chemical Company, unpublished results.

CONFIDENTIAL
Security Classification

**DOCUMENT CONTROL DATA - R&D**

*(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)*

| | |
|---|---|
| 1 ORIGINATING ACTIVITY (Corporate author) The Dow Chemical Company Midland, Michigan 48640 | 2a REPORT SECURITY CLASSIFICATION Confidential<br>2b GROUP IV |
| 3 REPORT TITLE Final Progress Report | |
| 4 DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Progress Report 1 January 1967 to 30 June 1969 | |
| 5 AUTHOR(S) (Last name, first name, initial) Sinke, G. C. and Stull, D. R. | |
| 6 REPORT DATE July 1969 | 7a TOTAL NO OF PAGES 24<br>7b NO OF REFS 6 |
| 8a CONTRACT OR GRANT NO F04611-67-C-0025<br>b PROJECT NO 3145<br>c BPSN-623148<br>Program Structure 750 G<br>d | 9a ORIGINATOR'S REPORT NUMBER(S)<br>9b OTHER REPORT NO(S) (Any other numbers that may be assigned this report) AFRPL-TR-69-183 |
| 10 AVAILABILITY/LIMITATION NOTICES This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of AFRPL(RPPR-STINFO) Edwards, California 93523. | |
| 11 SUPPLEMENTARY NOTES | 12 SPONSORING MILITARY ACTIVITY AFRPL, RTD Edwards Air Force Base, California |

13 ABSTRACT


The heats of formation of methylene bisoxyamine ~~($CH_6N_2O_2$)~~ and methylene bisoxyamine diperchlorate ~~($CH_6N_2O_2 \cdot 2HClO_4$)~~ were derived from oxygen bomb combustion calorimetry and solution calorimetry. Selected best values for the two compounds are -22.6 kcal/mole for liquid methylene bisoxyamine and -103.0 kcal/mole for crystalline methylene bisoxyamine diperchlorate.

A technique for obtaining heats of formation of gaseous C-H-O-N-F compounds was developed, with $CF_3CN$ as a reference substance. When the technique was applied to $F_2C(ONF_2)_2$, results deviated widely from the expected range. Chromatographic examination revealed a large fraction of $F_3CONF_2$ was present in the sample and no accurate result for $F_2C(ONF_2)_2$ could be derived. The amount of sample available was too small to allow purification.


DD FORM 1 JAN 64 1473

CONFIDENTIAL
Security Classification

CONFIDENTIAL
Security Classification

| 14. KEY WORDS | LINK A | | LINK B | | LINK C | |
|---|---|---|---|---|---|---|
| | ROLE | WT | ROLE | WT | ROLE | WT |
| Heat of formation | | | | | | |
| Heat of combustion | | | | | | |
| Methylene bisoxyamine | | | | | | |
| Methylene bisoxyamine diperchlorate | | | | | | |

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization *(corporate author)* issuing the report.

2a. REPORT SECURITY CLASSIFICATION. Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers *(either by the originator or by the sponsor)*, also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through ________________."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through ________________."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through ________________."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring *(paying for)* the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS)*, *(S)*, *(C)*, or *(U)*

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.

CONFIDENTIAL
Security Classification